

UNCLASSIFIED

AD _____

DEFENSE DOCUMENTATION CENTER

FOR

SCIENTIFIC AND TECHNICAL INFORMATION

CAMERON STATION ALEXANDRIA, VIRGINIA

DOWNGRADED AT 3 YEAR INTERVALS:
DECLASSIFIED AFTER 12 YEARS
DCD DIR 5200.10



UNCLASSIFIED

THIS REPORT HAS BEEN DECLASSIFIED
AND CLEARED FOR PUBLIC RELEASE.

DISTRIBUTION A
APPROVED FOR PUBLIC RELEASE;
DISTRIBUTION UNLIMITED.

AD No. 9923
ASTIA FILE COPY

EXPERIMENTAL DETERMINATION OF EVEN-ODD CHARACTER
OF EXCITED ELECTRONIC STATES OF MOLECULES WITH A
CENTER OF SYMMETRY

John R. Platt

Physics Department

University of Chicago, Chicago, Ill.

Abstract

Even-even transition intensities increase with mono-substitution but decrease with opposed disubstitution. Even-odd transition intensities which increase with monosubstitution must increase further with opposed disubstitution.

Determination of parity in this way may settle disputed assignments. Thus the ${}^1A_{1g} - {}^1E_{2g}$ π -transition of benzene is probably at 1700 Å. The first singlet absorption of naphthalene is ${}^1A_{1g} - {}^1E_{1u}$ or ${}^1A_{1g} - {}^1B_{2u}$ and cannot be ${}^1A_{1g} - {}^1A_{1g}$ even though the cancellation of transition matrix elements (from configuration interaction, in the one-electron approximation) gives it an intensity and vibrational structure similar to those in a forbidden transition. The visible bands of porphine are even-odd ($a_{2u} \rightarrow e_g$ ${}^1A_g - {}^1Q_u$).

Intensities in the 2100 Å transition of phenyl derivatives are being remeasured to settle its assignment in benzene, since existing data give conflicting results.

* * * * *

In molecules with a center of symmetry, transitions from an even ground state to an even excited state are forbidden, but may become allowed if substitution perturbs the symmetry. The intensity of the observed absorption then increases, especially in the 0-0

vibrational band. However, disubstitution by the same substituents at exactly opposite positions restores the symmetry and reduces the intensity again to nearly its original value if the vibrational interaction which makes the absorption visible is not too greatly altered by the substitution. The "spectroscopic moments"¹ of equal

¹J. R. Platt, J. Chem. Phys. 19, 263 (1951).

substituents at opposed positions therefore exactly cancel for an even-even transition.

Similarly, by first-order perturbation theory, the spectroscopic moments of equal substituents at opposed positions must add for an even-odd transition, giving approximately four times the intensity change produced by one substituent alone.¹

These differences make possible the unambiguous determination of the parity of every spectroscopically-observed excited state of a centrally-symmetric molecule. In many cases, this information alone will settle disputes over assignment of the states to theoretically-predicted wavefunctions.²

²J. R. Platt, J. Chem. Phys. 19, 101 (1951), esp. pp. 115-6.

Thus, the 2100 Å transition of benzene which was long assigned as ${}^1A_{1g} - {}^1B_{1u}$ ³ has recently been proposed to be ${}^1A_{1g} - {}^1E_{2g}$.⁴

³C. C. J. Roothaan and R. S. Mulliken, J. Chem. Phys. 16, 118 (1948).

⁴D. P. Craig, Proc. Roy. Soc. 200, 401 (1950); R. G. Parr, D. P. Craig and I. G. Ross, J. Chem. Phys. 18, 1561 (1950).

This proposal has been made in the implicit faith that certain approximate energy level calculations including configuration interaction must give the correct sequence of excited states; even though the absolute values of energies given by calculations of this kind are frequently in error by 2 ev. and more and the differences between the different approximations used by different computers are often much greater than this.⁴

Unfortunately the available data in the literature on intensities of the corresponding transitions in mono- and di-substituted benzenes with moderately strong substituents such as OH, NH₂ and COOH are scanty and conflicting. They are also partially invalidated by use of polar solvents at unspecified pH values. We are now engaged at this laboratory in remeasuring some of these intensities in non-polar solvents in order to settle the assignment of this transition.

Pending the outcome of these measurements, it seems more likely that the forbidden $^1A_{1g} - ^1E_{2g}$ phenyl π -electron transition is the relatively weak peak near 1700-1730 Å. which is not clearly seen in benzene itself but appears in toluene and in o- and m-xylene, becoming weak again with opposed disubstitution in p-xylene.⁵ Such intensity behavior indicates that the observed peak is probably

⁵J. R. Platt and H. B. Klevens, Chem. Rev. 41, 301 (1947).

even-even, supporting this assignment, which was proposed for it earlier⁶ because it lay on a smooth sequence with the other even-

⁶J. R. Platt, J. Chem. Phys. 17, 484 (1949), esp. p. 491.

even $e \rightarrow g$ ${}^1A - {}^1C_b$ transitions⁶ in naphthalene and anthracene which showed the same kind of increase of intensity with loss of central symmetry.

The intensity of this 1730 Å peak (f about 0.3 in the xylenes) seems to great for a Rydberg transition (f about 0.03 in ethylene⁷),

⁷J. R. Platt, H. B. Klevens and W. C. Price, J. Chem. Phys. 17, 466 (1949).

especially an even-even one, but is reasonable for an even-even π -electron transition.⁶ And its position is within 2,000 cm^{-1} of the position predicted for ${}^1A_{1g} - {}^1E_{2g}$ by either the free-electron or the LCAO-overlap method (with $\rho_{\text{spect}} = 20,000 \text{ cm}^{-1}$; and assuming the singlet-triplet separation is 4000-10000 cm^{-1}). This is significant because these methods are successful to this accuracy in predicting some 50 excited states of other ring systems.^{6,8,9}

⁸H. B. Klevens and J. R. Platt, J. Chem. Phys. 17, 470 (1949).

⁹J. R. Platt, J. Chem. Phys. 18, 1169 (1950).

Similarly, the lowest singlet transition in naphthalene is certainly even-odd as shown by its increases of intensity in 1,5- and 2,6-dichloronaphthalenes.¹ This confirms its assignment as ${}^1A_{1g} - {}^1E_{1u}$ ¹⁰ or ${}^1A - {}^1L_b$ ⁶ (or possibly ${}^1A_{1g} - {}^1B_{2u}$ ¹⁰) and makes impossible its assignment as ${}^1A_{1g} - {}^1A_{1g}$,¹¹ in spite of its

¹⁰J. Jacobs, Proc. Phys. Soc. (Lond.) 62, 710 (1949).

¹¹D. P. Craig, Disc. Far. Soc. 9, 5 (1951).

low intensity and apparently forbidden type of vibrational structure.

¹² This shows clearly that the "accidental" cancellation of tran-

¹²H. Spöner, private communication.

sition matrix elements in a formally-allowed one-electron transition (such as this one is if it is even-odd), due to the effect of configuration interaction¹⁰ in producing a high "effective angular momentum" in the excited state,⁶ can make such an allowed transition mimic the appearance of a forbidden one not only in its low intensity but also in its vibrational structure. Therefore, in a complex molecule neither the intensity nor structure can be relied on for proof that an observed transition would not be formally allowed in the one-electron approximation. Since the theoretically-predicted energies or sequence of energies are evidently also no more than a rough guide in assignments, the perturbation method, or comparison method, emerges as an especially useful guide to classification of electronic states, at least when the observed changes can be interpreted, as in these cases.

The visible bands of porphine are believed to represent another case of a formally-allowed one-electron transition which is relatively weak and presumably "accidentally" forbidden by the same mechanism^{13,14,15} and which has a weak 0-0 band (especially

¹³W. T. Simpson, J. Chem. Phys. 17, 1218 (1949).

¹⁴H. Kuhn, Chimia 4, 203 (1950).

¹⁵H. C. Longuet-Higgins, C. W. Rector, and J. R. Platt, J. Chem. Phys. 18, 1174 (1950).

in the salts or hydrochlorides,¹⁶ where the D_{4h} symmetry is strictly

¹⁶J. G. Erdman and A. H. Corwin, J. Am. Chem. Soc. 68, 1835 (1946).

obtained) but which is nevertheless certainly even-odd, as shown by di- and poly- substitution effects on intensities in the porphyrins.¹⁷ If we treat the removal of a double bond from the

¹⁷J. R. Platt, "Electronic Structure and Excitation of Polyenes and Porphyrins", Chapter 4 of Volume III of "Radiation Biology", ed. Sterling Hendricks, McGraw-Hill, in press.

porphine ring as a perturbation, the addition of the resultant spectroscopic moments for bacteriochlorophyll, with two opposite double bonds removed, accounts for the fact that its first red band is about four times as intense as the first band in the chlorins which have only one double bond removed. This demonstrates the even-odd character of the transition and shows the approximate validity, even with these drastic changes, of the first-order perturbation theory.